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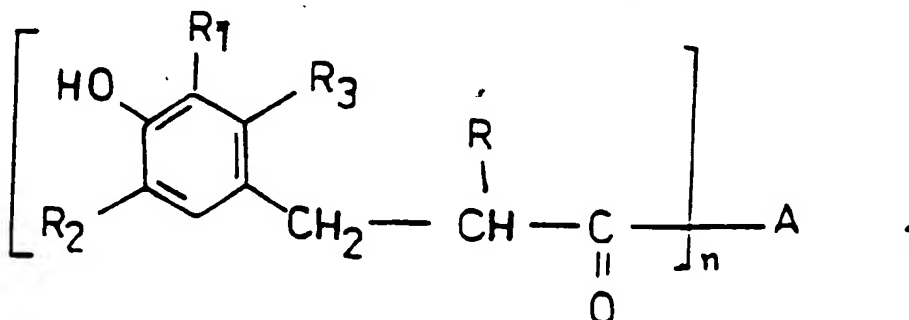
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(54) Stabilizers for organic materials.

(57) The invention relates to a stabilizer for organic materials, which are liable to oxidative and/or thermal decomposition under influence of actinic irradiation of formula 1, wherein R is hydrogen or a methyl group R₁ and R₂, which may be the same, or different represent a tertiary alkyl group having 4-8 C-atoms, R₃ is hydrogen or a methyl group, n = 2 and A a polyol having 3 to 6 C-atoms or a di-polyol containing 6-12 C-atoms.



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The invention relates to novel stabilizers for organic materials which are liable to oxidative and/or thermal decomposition and/or decomposition under influence of actinic irradiation, such as petroleum products, e.g. lubricating oils and lubricating greases, and plastics, such as polyvinylchloride, polyalkylenes and polystyrene.

5 In order to prevent oxidative and/or thermal decomposition (degradation) of petroleum products and plastics, such as polyvinylchloride, polyalkylenes and polystyrene, on large scale antioxidants and antioxidants are used, which dependent on their chemical construction, inhibit the initiation or propagation of oxidation reactions. Especially as antioxidants that inhibit the propagation of oxidation reactions, secondary alkylaryl- and diarylamines and, in particular, hindered phenols are applied (vide Kirk-Othmer, Encyclopedia
10 of Chemical Technology, 3rd edition part 3, page 128-148 and in particular pages 130-133).

In order to prevent decomposition under influence of actinic irradiation, in particular decomposition under influence of UV-irradiation, often so-called HALs (hindered amine light stabilizers) are applied, the most important ones of which are 2,2,6,6-tetramethyl-4-piperidinol and carboxylic acids, such as bis-(2,2,6,6-tetramethyl-4-piperidinyl)sebacate and - azelate, which are especially active in polypropylene,
15 polyethylene, styrene polymers, polyurethanes and coatings containing acrylic polymer (vide Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, volume 23, page 615-627 and in particular pages 620-621 and page 624).

Although said compounds generally have good properties, continuously novel compounds of these types are developed, in order to meet the higher and higher requirements with respect to the stability of
20 petroleum products (e.g. lubricating oil) and of polymers.

So in EP-A-89119641.2 (publication no. 366 040) hindered phenol antioxidants of formula 1 are described, wherein R is a methyl group, R₁ is an alkyl, cycloalkyl, phenyl, or aralkyl group, R₂ is hydrogen or an alkyl, cycloalkyl, phenyl or aralkyl group, R₃ is hydrogen or a methyl group, n is an integer of 1-4 or 6, wherein, if n = 2, A is preferably an alkylene dioxy group having 2-8 carbon atoms or an alkylene dioxy
25 group interrupted by ether oxygen or a thio group.

In EP-A-88108282.0 (publ. no. 300160) the ester of 2,2,6,6-tetramethyl-4-piperidinol and behenic acid is described, which serves as stabilizer against the decomposition of polymers by actinic irradiation.

Now the object of the invention is to provide novel stabilizers with particularly favourable, improved properties.

30 According to a first aspect of the invention, novel compounds of formula 1 are provided, wherein R is hydrogen or a methyl group, R₁ and R₂, which may be the same or different, represent a tertiary alkyl group having 4-8 carbon atoms, R₃ is hydrogen or a methyl group, n = 2 and A is a polyol having 3-6 C-atoms, or a dipolyol having 6-12 C-atoms.

35 Compared to the known stabilizers of this type, these novel compounds have improved properties with respect to the stabilization against thermal and oxidative degradation of both petroleum products and plastics.

In the novel compounds of formula 1, R₁ and R₂ preferably both are a tertiary butyl group. The tertiary butyl group provides an excellent sterical hindering of the hydroxyl group of the phenol and is extremely stable itself, so that the compounds have an optimum stabilizing effect.

40 The polyol or di-polyol group (A) has at least one free hydroxyl group, which also contributes to the stabilizing effect of the compounds.

Preferably A is a glycerol or di-glycerol moiety. The stabilizing effect of the compound is then excellent, while the compounds themselves are stable.

45 According to the number of free hydroxyl groups of the polyol or dipolyol moiety is higher, the long term thermal stability improves, but this is at the expense of the colour stability of the compounds.

According to another aspect of the invention novel compounds of formula 4 are provided, wherein R₄ and R₅, which may be the same or different, may represent an optionally branched alkylene group having 1-8 C-atoms.

50 These compounds have a stabilizing effect both against thermal and oxidative degradation and against decomposition or degradation under influence of actinic irradiation, in particular UV-irradiation. So these are stabilizers with combined antioxidant/light stabilizer properties.

Preferably at least one of the groups R₄ and R₅ is an ethylene or 1-methylethylene (propylene) group. In that case the compounds are bis esters of thiodipropionic acid or thiodiisobutyric acid, which may be easily prepared, have a good stability themselves and provide an optimum stabilizing effect.

55 The novel stabilizers are included in usual amounts in the petroleum products or plastics to be stabilized that is to say amounts of 0.1-10 and preferably 0.05-5% by weight. Optimal results are generally obtained with 0.1-3 and in particular with 1-3 % by weight.

The invention is further elucidated by the following examples.

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Example I

Preparation of diglyceryl-bis[β -(3,5-di-tertiary butyl-4-hydroxyphenyl)propionic ester] (reaction scheme A, formula 5).

A three-neck flask with stirrer, thermometer and cooler is filled with :

40 g (0.137 moles)	β -(3,5-di-tertiary butyl-4-hydroxy phenyl)-propionic acid methyl ester (I)
12.95 g (0.078 mol)	diglycerine (II)
2 g	titanium butoxide

The reaction mixture was heated at 160 ° C for 5 hours, while the methanol formed with the reaction was continuously removed by means of distillation. Subsequently the reaction mixture was cooled down. The brown-coloured residue was incorporated into the ether. The ether layer was washed with water and dried whereafter the ether was distilled. The residue was dissolved in ethanol and purified over a column of silica gel. After distilling the ethanol a yellow-coloured viscous liquid was obtained.

Yield: 39.6 g = 85%

The NMR spectrum is in accordance with formula 5.

Example II

Preparation of thiodipropionic acid bis (2,2,6,6-tetramethyl-4-piperidinyl ester) (reaction scheme B; formula 6).

A three neck-flask with stirrer, thermometer and cooler is filled with:

10.3 g (0.05 mole) thiodipropionic acid dimethyl ester (IV)

15.7 g (0.1 mole) 2,2,6,6-tetramethyl-4-piperidinol (V)

150 ml toluene

1 g titanium butoxide

The reaction mixture was heated for 8 hours at reflux temperature.

During this period about 500 ml of toluene was distilled and at the same time replaced by fresh toluene.

After the reflux period the reaction mixture was cooled down and washed with water. The remaining toluene solution was dried and filtered. After distilling the toluene a substantially colourless viscous liquid was obtained.

Yield: 21 g = 92%

From the NMR-spectrum it follows, that this viscous liquid substantially consists of the compound of formula 6.

Example III

The compounds according to example I and example II were applied as stabilizer in a softener-free, calcium-zinc-stabilized PVC composition

S-PVC (K=68-70)	100 parts by weight
Paraloid KM-334 (Impact-strenght additive)	5-8 parts by weight
Paraloid K-120N (Flow improver)	0.5-1.5 parts by weight
Hydrocarb 95T (chalk)	3-10 parts by weight
Titanium dioxide (Kronos-2220)	3-10 parts by weight
Ca/Zn stabilizer	3.5-4.5 parts by weight
Stabilizer (oxyd/therm., UV)	1-3 parts by weight

Test plates of this composition which contain the stabilizer according to example I were tested on their colour stability, and compared with test plates with an analogous composition wherein only β -(3,5-di-t-butyl-4-hydroxyphenyl)propionic-n-octadecyl ester were applied.

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The colour stability with the stabilizer of Example I was, when applied in amounts between 1 and 3 parts by weight (on 100 parts by weight of PVC), in any case better than with the comparative stabilizer.

Test plates of this composition which contain the stabilizer of Example II, and test plates which contain the β -(3,5-di-*t*-butyl-4-hydroxyphenyl)propionic acid-*n*-octadecyl ester, were tested on their light stability with the aid of an apparatus for artificial exposure, QUV panel, lamp A.

The light stability with the stabilizer of example II was, when applied in amounts between 1 and 3 (on 100 parts by weight of PVC), in any case better than with the comparative stabilizer.

Example IV

The compounds according to example I and II were applied as stabiliser in a softener containing film composition stabilized with Ba/Zn:

S-PVC (K = 65)	100 parts by weight
Softener (DOP)	20-25 parts by weight
Epoxized soy bean oil	2-3 parts by weight
Titanium dioxide	5-10 parts by weight
Stabilizer	1.5-3 parts by weight

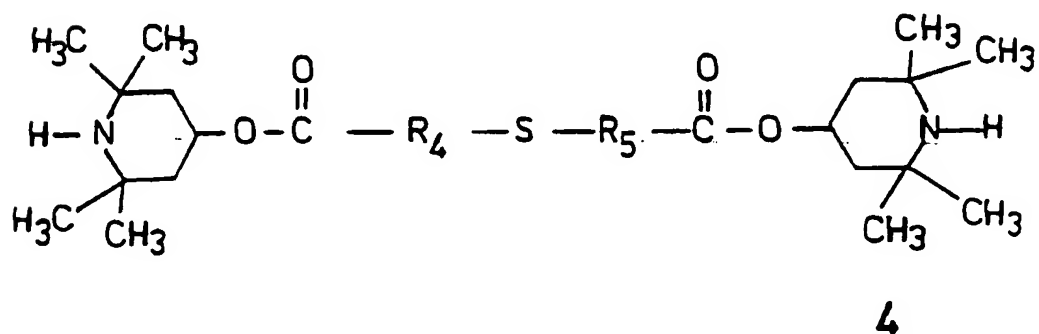
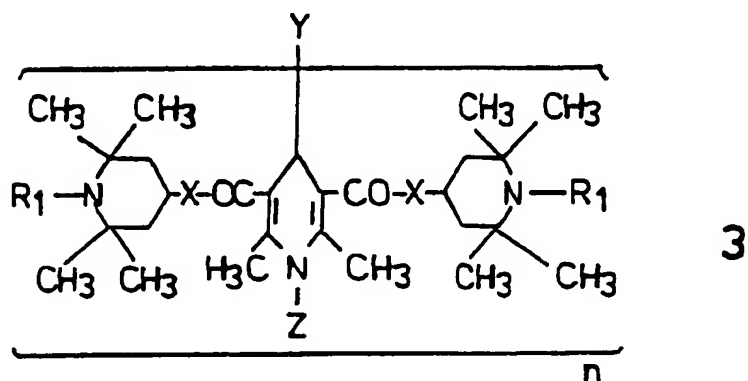
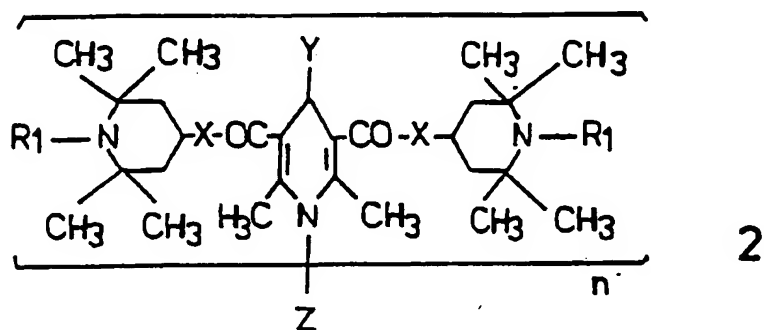
Test films of this composition which contain the stabilizer of example I and films which contain a usual stabilizer pentaerythritol-tetra [β -3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate] were tested on their resistance against thermal and oxidative degradation and the yellow coloration after the test was measured with a CIE Lab colour measuring system, manufacturer Dr. Lange.

The yellow coloration of the films with the stabilizer of Example I was less than that of the films which contain the usual stabilizer.

Test films of this composition which contain the stabilizer of Example II, upon measuring the light stability with the artificial exposing apparatus QUV panel, lamp A, provide a better result than similar films which contain a corresponding amount of the usual stabilizer.

Claims

1. Stabilizer for organic materials which are liable to oxidative and/or thermal decomposition and/or decomposition under influence of actinic irradiation, of formula 1, wherein R is hydrogen or a methyl group, R₁ and R₂ which may be the same or different, represent a tertiary alkyl group having 4-8 C-atoms, R₃ is hydrogen or a methyl group, n = 2 and A is a polyol having 3-6 C-atoms or a di-polyol having 6-12 C-atoms.
2. Stabilizer according to claim 1, wherein R₁ and R₂ both are a tertiary butyl group.
3. Stabilizer according to claim 1 or 2, wherein A is a glycerol or di-glycerol moiety.
4. Stabilizer according to claim 1 or 2, wherein A is a sorbitol or di-sorbitol moiety.
5. Stabilizer for organic materials which are liable to oxidative and/or thermal decomposition and/or decomposition under influence of actinic irradiation, of formula 4, wherein R₄ and R₅ which may be the same or different, represent an optionally branched alkylene group having 1-8 carbon atoms.
6. Stabilizer according to claim 5, wherein at least one of the groups R₄ and R₅ is an ethylene or 1-methylethylene group (propylene group).
7. Stabilizer according to claim 6, wherein R₄ and R₅ both are an ethylene group.
8. Stabilizer according to claim 6, wherein R₄ and R₅ both are a 1-methylethylene group.
9. Petroleum product or plastic material stabilized against oxidative and/or thermal decomposition and/or decomposition under influence of actinic irradiation, characterized in that it contains a compound according to any one of the preceding claims as stabilizer.

$$\left[\begin{array}{c} \text{R}_1 \\ | \\ \text{HO} - \text{C}_6\text{H}_3 - \text{R}_3 \\ | \\ \text{R}_2 \end{array} \text{CH}_2 - \text{CH} \begin{array}{c} | \\ \text{R} \end{array} - \text{C} \begin{array}{c} || \\ \text{O} \end{array} \right]_n \text{A} \quad (1)$$


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